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TI - PRODUCTION OF SURFACE-TREATED ARTICLE
IN - HINO MAMORU; BESSHO TOMOYUKI; YUASA MOTOKAZU
PA - SEKISUI CHEMICAL CO LTD
IC - C23C14/56 ; C23C16/40 ; C23C16/42 ; C23C16/50 ; C23C16/54 ;
C08J7/00

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TI - Base material surface processing method - involves supplying process gas between counter electrodes and generating discharge plasma to form coating film on base material which is conveyed between counter electrodes

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PA - (SEKI) SEKISUI CHEM IND CO LTD

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AB - JP11241165 NOVELTY - Electric field of strength 1-100 kV/cm is applied between mutually opposing electrodes (30, 31, 40, 41) for 100 μ s or less under atmospheric pressure and a discharge plasma is generated. A continuous base material (12) is conveyed between the counter electrodes and process gas is introduced between the electrodes so that coating film is formed on the base surface, by plasma treatment.

- USE - For forming various coating films such as anti-reflective coating, antistatic film, electromagnetic shield film, infrared rays reflective film, etc., on base material utilized domestic and industrial applications, semiconductor devices.
- ADVANTAGE - High quality and uniform coating film is formed at normal atmospheric pressure, thus large exhaust system is unnecessary. Operation property and economical efficiency of production are improved.
- DESCRIPTION OF DRAWING - The figure shows model diagram of processing apparatus. (12) Base material; (30, 31, 40, 41) Opposing electrodes.
- (Dwg.3/5)

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PA - SEKISUI CHEM CO LTD

TI - PRODUCTION OF SURFACE-TREATED ARTICLE

AB - PROBLEM TO BE SOLVED: To provide a method for producing a laminated body capable of continuously film-forming on one side of a base material under the pressure in the vicinity of the atmospheric pressure and excellent in the uniformity of film thickness and film quality and moreover to provide a method for producing a surface-treated article excellent in adhesion between a thin film, a base material or the like.

- SOLUTION: Gases 90 and 91 for treating are introduced into the spaces of counter electrodes 30/40 and 31/41 in which at least either counter face is set with solid dielectrics 60 to 62 to regulate the pressure to the one in the vicinity of the atmospheric pressure, and the electric fields made into pulse in which the voltage rise time is regulated to $\leq 100 \mu s$, and the electric field strength is regulated to 1 to 100 kV/cm are applied to the spaces between the counter electrodes 30/40 and 31/41 to generate discharge plasma, and moreover, between the counter electrodes 30/40 and 31/41, a substrate 12 is continuously passed through so as to be adhered to either counter face 30 or 31. The substrate or the face laminated with at least one kind of thin film is previously subjected to plasma treatment.

SI - C08J7/00

I - C23C14/56 ; C23C16/40 ; C23C16/42 ; C23C16/50 ; C23C16/54

* NOTICES *

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2. **** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of a surface treatment article.

[0002]

[Description of the Prior Art] Although the base material which consists of plastics, a metal, paper, fiber, etc. is widely used as home use and an industrial use material, if specific functions, such as an electrical property, an optical property, and a mechanical characteristic, are given to the front face, the use is expanded further and it comes to have big added value.

[0003] As a method of manufacturing the surface treatment article which comes to carry out the laminating of the thin film which gave the specific function to the front face of the above base materials, a vacuum deposition method, the sputtering method, the ion beam method, the ion plating method, the plasma CVD method using the glow discharge under reduced pressure, etc. are learned. However, each of these methods is performed by the vacuum system, large-scale facilities, such as a vacuum chamber and a large-sized vacuum pump, are required for them, and there are various kinds of limitations in manufacture.

[0004] In order to form a thin film in the front face of a long base material by the vacuum system, two kinds, a batch method and a continuous method, are in manufacture. In a batch method, thin film formation is performed by reduced pressure and the closed system, the roll which wound the base material around the long picture is put into a vacuum chamber, and a thin film is formed by the front face, beginning to roll a base material from a roll in this. By this method, vacuum release and vacuum formation must be repeated for every carrying in of a raw material or taking out of a product, and with the size of a facility, since a limitation appears in the capacity of the diameter of a base-material roll, a thin film raw material, etc., productive efficiency also becomes bad.

[0005] In a continuous method, in order to acquire a reduced pressure state, a differential-pumping method is used, and it exhausts gradually down to reduced pressure from atmospheric pressure, and a thin film is formed all over the space which held continuously the degree of vacuum required for membrane formation of a thin film. Although this method is easy for carrying in and a raw material supplement of a roll base material, since it is necessary to exhaust beyond the inflow of the air into a thin film deposition system, and to hold a degree of vacuum, a mass vacuum pump is needed and growing gigantic of a facility is not avoided.

[0006] Moreover, when giving two or more functions to one base material or adding a more advanced function, the attempt which carries out the laminating of two or more sorts of thin films is made. However, when forming a multilayer industrially, in order to have to repeat the cycle of release of the membrane formation-vacuum of a vacuum formation-thin film for every kind of layer in a batch method, it is very inefficient and is not realistic. Moreover, in a continuous method, a large-scale facility is required also of a monolayer, and introduction of the process of multilayer formation is difficult. Furthermore, correspondence of a little variety was difficult for the continuous method on plant-and-equipment investment, and the correspondence to the use which adds a specific function to a base material separately etc. was very difficult.

[0007] A proposal various in the method of manufacturing the above surface treatment articles is made. in JP,2-181701,A and a number (***** 3-518202) official report Although the method of

controlling the degree of incident angle of an electron gun and the angle of a vacuum evaporation roll and the source of vacuum evaporation, and forming a cascade screen on the surface of a base material in a vacuum deposition method is proposed. The batch method had to be adopted having consented to the very inefficient thing, since plant-and-equipment investment became excessive too much for carrying out by there being no change in the continuous method using the differential-pumping method.

[0008] Furthermore, a facility, such as carrying out design control of the source of vacuum evaporation and the position of a base material very strictly, in order to make membrane quality uniform for improvement in acid resisting, when forming a thin film only in one side of a base material, protecting a base material or preparing a baffle, in order to prevent an emission turning to the rear face of a base material further, was enlarged.

[0009]

[Problem(s) to be Solved by the Invention] It is in offering the manufacture method of a surface treatment article of this invention having solved the above-mentioned technical problem, and the 1st purpose having been continuously produced on one side of a base material under the pressure near the atmospheric pressure, and having excelled in thickness and membrane homogeneity, and the 2nd purpose is in offering the manufacture method of a surface treatment article excellent in the adhesion of a thin film, a base material, etc.

[0010]

[Means for Solving the Problem] The manufacture method (henceforth a "this invention") of a surface treatment article according to claim 1. The gas for processing is introduced between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side. When voltage build up time impresses and field strength impresses the pulse-sized 1-100kV [/cm] electric field 100 or less microseconds between the pressure near the atmospheric pressure, nothing, and a counterelectrode, while generating electric discharge plasma. Between the aforementioned counterelectrodes, it continues, and a base material is stuck to one of opposite sides, and is passed.

[0011] In this invention, the bottom of the pressure near the atmospheric pressure means the bottom of the pressure of 13.3-106.4kPa, pressure regulation is easy, and the range of 93.1-103.74kPa to which equipment becomes simple is desirable.

[0012] Under the pressure near the atmospheric pressure, shifting to an arc discharge state in an instant is known except specific gas, such as helium and a ketone, without holding the stable plasma electric discharge state. However, if the pulse-sized electric field are impressed, before shifting to arc discharge, electric discharge can be stopped, and it realizes, and the cycle of starting electric discharge again can be stabilized and can generate electric discharge plasma.

[0013] According to the method of impressing the pulse-sized specific electric field in this invention, it is possible to generate electric discharge plasma regardless of the kind of gas which exists all over plasma generating space. Although it was indispensable to have performed processing using electric discharge plasma also under well-known low voltage conditions conventionally within the airtight container intercepted from the open air under a specific gas atmosphere, according to this invention, an open system or the low airtight system of the grade which prevents a free gaseous spill can also be carried out, and the high-density plasma state can be realized.

[0014] In this invention, the gas molecule to which field strength exists all over plasma generating space by 1 - 100 kV/cm by impressing the pulse electric field of 100 or less microseconds in build up time in which it has a steep standup excites efficiently. It is difficult to ionize efficiently the molecule which excites to level with the higher molecule already ionized when excitation of a molecule small [of the molecule which is equivalent to supplying gradually the energy which has the size from which impressing pulse electric field with a late standup differs, and is first ionized by low energy i.e., the first ionization potential,] takes place preferentially and energy high next is supplied, and exists all over plasma generating space. On the other hand, according to the pulse electric field whose build up time is 100 or less microseconds, it is equivalent to giving energy to the molecule which exists all over space all at once, the absolute number of the molecule in the state where it ionized in space increases, and plasma density becomes a bird clapper highly.

[0015] When it installs a solid dielectric in one side of the above-mentioned electrode, the part which electric discharge plasma generates is the space between solid dielectrics between a solid dielectric

and an electrode, when a solid dielectric is installed in the both sides of the above-mentioned electrode.

[0016] As an electrode, what consists of alloys, such as metal simple substances, such as copper and aluminum, stainless steel, and brass, an intermetallic compound, etc. is mentioned, for example. In order to avoid generating of the arc discharge by electric-field concentration, as for a counterelectrode, it is desirable that it is the structure where the distance between counterelectrodes serves as abbreviation regularity. As electrode structure of fulfilling this condition, an parallel monotonous type, a hyperboloid opposite monotonous type, coaxial-circles telescopic structure, etc. are mentioned. Since there is a possibility that arc discharge may occur at the end that an electrode edge is sharp, as for an edge, it is desirable to have carried out taper processing.

[0017] As a solid dielectric, it installs in one side or the both sides of an opposite side of an electrode. Under the present circumstances, a solid dielectric and the electrode of the side installed stick, and are wearing the opposite side of the touching electrode completely. If there is a part which electrodes counter directly, without being covered by the solid dielectric, arc discharge will arise from there.

[0018] As a solid dielectric, multiple oxides, such as metallic oxides, such as plastics, such as a polytetrafluoroethylene and a polyethylene terephthalate, glass, a silicon dioxide, an aluminum oxide, a zirconium dioxide, and a titanium dioxide, and a barium titanate, etc. are mentioned, for example.

[0019] Although the shape of the shape of a sheet and a film has as the configuration of a solid dielectric, it is desirable that thickness is 0.05-4mm. The high voltage is taken to generate electric discharge plasma, if too thick, if too thin, dielectric breakdown will happen at the time of voltage impression, and arc discharge will occur.

[0020] Moreover, as for a solid dielectric, it is desirable that specific inductive capacity is two (bottom of the 25 degreeC environment, following **) or more. Specific inductive capacity can mention a polytetrafluoroethylene, glass, the film that consists of a metallic oxide as an example of two or more dielectrics, for example. Furthermore, in order to be stabilized and to generate high-density electric discharge plasma, specific inductive capacity of things is desirable using ten or more fixed dielectrics. Although especially the upper limit of specific inductive capacity is not limited, about 18,500 thing is known for an actual material. It is desirable for specific inductive capacity to consist of a metallic-oxide thin film mixed with 5 - 50 % of the weight of oxidization titanium and 50 - 95 % of the weight of aluminum oxides or a metallic-oxide thin film containing a zirconium oxide as ten or more solid dielectrics, and to use that whose thickness of the thin film is 10-1000 micrometers.

[0021] Although an inter-electrode distance is determined in consideration of the purpose using the thickness of a solid dielectric, the size of applied voltage, and plasma etc., it is desirable that it is 1-50mm. In less than 1mm, if it is difficult for an inter-electrode distance to be too small and to pass a base material etc. and it exceeds 50mm, it will become difficult to generate uniform glow discharge plasma.

[0022] In this invention, the electric field impressed to the above-mentioned inter-electrode one are pulse-ized, voltage build up time is made and field strength is made with 1 - 100 kV/cm 100 or less microseconds.

[0023] The example of a pulse-voltage wave is shown in drawing 1 . A wave (A) and (B) are [a square wave type and the wave (D) of an impulse type and a wave (C)] become [irregular] type waves. Although voltage impression mentioned what is the repeat of positive/negative to drawing 1 , you may use the so-called wave of the piece sinuate which impresses voltage to a positive or negative polarity [one of] side.

[0024] Although the pulse-voltage wave in this invention is not limited to the wave mentioned here, ionization of the gas in the case of plasma generating is efficiently performed, so that the build up time of a pulse is short. When the build up time of a pulse exceeds 100 microseconds, an electric discharge state will become being easy to shift to an arc unstable, and it will become impossible to expect the high-density plasma state by pulse electric field. Moreover, although the earlier one of build up time is good, it is difficult for the equipment which has the field strength of the size which is the grade which plasma generates in an ordinary pressure, and is made to generate electric field with

early build up time to have restrictions, and to realize the pulse electric field of the build up time for less than 40ns actually. 50ns - 5 microseconds of build up time are more desirable. In addition, build up time here means time for voltage change to be positive continuously.

[0025] Moreover, the falling time of pulse electric field also has a steep desirable thing, and it is desirable that it is the same time scale for 100 or less microseconds as build up time. Although it changes also with pulse electric-field generating technology, by the power unit used in the example of this invention, it falls with build up time and time can set it as the same time, for example.

[0026] Furthermore, you may become irregular using pulse shape, build up time, and the pulse from which frequency differs.

[0027] The above-mentioned electric discharge is performed by impression of voltage. Although the size of voltage is decided suitably, it is made into the range from which inter-electrode field strength serves as 1 - 100 kV/cm in this invention. Processing takes time too much as it is less than 1 kV/cm, and if 100 kV/cm is exceeded, it will become easy to generate arc discharge. In addition, the above-mentioned field strength says what ***(ed)** the value of the peak-peak of not an effective voltage but the voltage impressed to inter-electrode in inter-electrode distance. Moreover, in impression of a pulse voltage, you may superimpose a direct current.

[0028] As a power supply used for impression of such a pulse voltage, the thing of a publication is used [Japanese Patent Application No. / No. 186314 / nine to] /, for example.

[0029] Setting to the electric discharge obtained by the above-mentioned method, the discharge current density between counterelectrodes is 0.2 - 300 mA/cm². Being made is desirable.

[0030] When the above-mentioned discharge current density means the value which ***(ed)** current value which flows to inter-electrode by electric discharge in the area of the direction which intersects perpendicularly with the flow direction of the current in discharge space and an parallel monotonous type thing is used as an electrode, it is equivalent to the value which ***(ed)** the above-mentioned current value in the opposite area. Although pulse-like current flows in this invention in order to form pulse electric field in inter-electrode, the value which ***(ed)** the maximum of the pulse current, i.e., peak to peak value, in the above-mentioned area in this case is said.

[0031] 0.2 which it is shown clearly by research of this invention persons that it is the value to which discharge current density influences manufacture of a surface treatment article reflecting plasma density, and described above inter-electrode discharge current density in the glow discharge under the pressure near the atmospheric pressure as shown below - 300 mA/cm² By considering as the range, uniform electric discharge plasma is generated and the manufacture result of a good surface treatment article can be obtained.

[0032] As a base material used for this invention, plastics, such as polyethylene, polypropylene, polystyrene, a polycarbonate, a polyethylene terephthalate, a polyphenylene ape fight, a polyether ether ketone, a polytetrafluoroethylene, and acrylic resin, glass, a ceramic, a metal, etc. are mentioned, for example. Especially as a configuration of a base material, although not limited, since it processes continuously, it is suitable for long picture type base materials, such as the shape of the shape of a tabular and a film, and a pipe.

[0033] In this invention, the laminating of arbitrary thin films is possible by selection of the gas (it is hereafter called the gas for processing) which exists not only in the metallic element content gas mentioned later but in electric discharge plasma generating space.

[0034] As gas for processing, by using fluorine content compound gas, a fluorine content machine can be made to be able to form in a base-material front face, surface energy can be made low, and a water-repellent front face can be obtained.

[0035] As a fluorine element content compound, fluorine-carbon compounds, such as 8 6 fluoride [propylene] (CF₃ CFCF₂), cyclobutane, etc. fluoride (C₄ F₈), are mentioned. 8 6 fluoride [propylene] and cyclobutane fluoride which do not generate the hydrogen fluoride which is harmful gas from a viewpoint on safe are used.

[0036] The method of introducing the gas for processing introduced between the counterelectrodes for each class by the well-known method, for example, blowing off the gas for processing with the gas supply vessel of the shape of a slit or a nozzle, the method of preparing the hole which supplies the gas for processing towards the request to the electrode which counters a base-material processing side, and blowing off this, a pump, a blower, and a blower are used, and the method of supplying and

circulating etc. is mentioned to inter-electrode.

[0037] Moreover, the polymerization film of a hydrophilic property can also be made to deposit in a molecule by processing under the atmosphere of the monomer which has a hydrophilic radical and a polymerization nature unsaturated bond. As the above-mentioned hydrophilic radical, hydrophilic radicals, such as a hydroxyl group, a sulfonic group, a sulfonate machine, the 1st class, the 2nd class or the 3rd class amino group, an amide group, a quarternary-ammonium-salt machine, a carboxylic-acid machine, and a carboxylate machine, etc. are mentioned. Moreover, even if it uses the monomer which has a polyethylene-glycol chain, a hydrophilic polymerization film can be deposited similarly.

[0038] As the above-mentioned monomer, acrylic-acid, methacrylic-acid, acrylamide, methacrylamide, N, and N-dimethyl acrylamide, acrylic-acid sodium, methacrylic-acid sodium, an acrylic-acid potassium, a methacrylic-acid potassium, styrene sulfonic-acid sodium, allyl alcohol, an allylamine, polyethylene-glycol dimethacrylate ester, polyethylene-glycol diacylic ester, etc. are mentioned, and these at least one sort can be used.

[0039] As this invention was indicated to the claim 2, by continuing, and sticking a base material to one of opposite sides, and passing it between the counterelectrodes which adjoined two or more sets and were prepared, for each class, a homotypic or a thin film of a different kind makes it deposit continuously one by one, and can manufacture a surface treatment article.

[0040] In this case, two or more sets of counterelectrodes adjoin, and are arranged, and it is carried out in the equipment with which the solid dielectric is installed in one [at least] opposite side of this counterelectrode. Therefore, the electric discharge plasma treatment equipment of each smallness unit of this invention does not need to have the same arrangement of the solid dielectric of all counterelectrodes, if the above-mentioned conditions are satisfied.

[0041] In this case, the field where the counterelectrode of each class is contained constitutes the electric discharge plasma treatment equipment of the small unit which became independent, respectively, it is supplied so that the gas for processing may serve as a pressure near the atmospheric pressure at this equipment, and by the well-known method, a base material is run the space between counterelectrodes continuously, and is introduced into the electric discharge plasma treatment equipment of the following small unit one by one.

[0042] As this invention was indicated to the claim 3, as for the pulse-ized electric field, it is desirable that 0.5-100kHz and pulse duration are made for frequency with 1 - 1000 microseconds.

[0043] For a low reason, time requires plasma density for processing too much as it is less than 0.5kHz, and if it exceeds 100kHz, arc discharge will become easy to generate the frequency of pulse electric field. More preferably, it is 1kHz or more and processing speed can be greatly raised by impressing the pulse electric field of such high frequency.

[0044] Moreover, the pulse duration in the above-mentioned pulse electric field will become easy to shift to arc discharge, if electric discharge becomes being less than 1 microsecond with an unstable thing and it exceeds 1000 microseconds. It is 3 microseconds - 200 microseconds more preferably. Here, although one pulse duration has shown the example in drawing 2, it means the time in the pulse electric field which consist of a repeat of ON and OFF for a pulse to continue. By intermission type pulse like drawing 2 (a), although pulse duration is equal to pulse width time, unlike pulse width time, in the pulse of a wave like drawing 2 (b), time including two or more of a series of pulses is said.

[0045] Furthermore, in order to stabilize electric discharge, it is desirable to have the OFF time continued for at least 1 microsecond in 1ms of charging time values.

[0046] As this invention was indicated to the claim 4, that in which the gas for processing introduced into any 1 or more sets of two or more sets of counterelectrodes contains metallic element content gas is desirable.

[0047] An electric discharge state cannot be easily stabilized by the atmosphere containing such metallic element content gas, and unless it is based on the method using the electric field by which this invention was pulse-ized, it cannot process. As the above-mentioned metal, for example aluminum, As, Au, B, Bi, Sb, calcium, Cd, Cr, Co, Cu, Fe, Ga, germanium, Hg, Hf, In, Ir, Li, Mg, Mn, Mo, Na, nickel, P, Pb, Po, Pt, Rh, Metals, such as Se, Si, Sn, Ta, Te, Ti, V, W, Y, Zn, and Zr, are mentioned, and the gas for processing, such as a metal organic compound, a metal-halogenated

compound, metal-hydride, a metal-halogenated compound, and a metal alkoxide, is mentioned as gas containing this metal.

[0048] When it specifically explains taking the case of the case where a metal is Si, a tetramethylsilane [Si (CH₃)₄], The organometallic compound; 4 silicon fluoride of dimethylsilane [Si (CH₃)₂ two H₂], a tetraethyl silane [Si (C₂ H₅)₄], etc. (SiF₄), Metal halogenated compounds, such as four silicon chlorides (SiCl₄) and two silicon chlorides (SiH₂ Cl₂); A mono silane (SiH₄), Metal hydride, such as a disilane (SiH₃ SiH₃) and trishiran (SiH₃ SiH₂ SiH₃); A tetramethoxy silane [Si (OCH₃)₄], The metal alkoxide of a tetrapod ethoxy silane [Si (OC two H₅)₄] etc. is mentioned, and these at least one sort including other metals can be used if needed. In the above-mentioned metal content gas, in consideration of safety, what does not have danger, such as ignition and explosion, in the ordinary temperature of a metal alkoxide metallurgy group halogenated compound etc. and the atmosphere is desirable, and a metal alkoxide is suitably used from the point of generating of corrosive and harmful gas.

[0049] What is necessary is just to introduce into discharge space through a vaporizer, if it has the shape of a liquid and a solid-state, although it can introduce into discharge space as it is, if the above-mentioned metal content gas is a gas.

[0050] It is more desirable than an atmosphere gas independent [the viewpoint of economical efficiency and safety to / above-mentioned / for processing] to process in the atmosphere thinned with dilution gas. As dilution gas, rare gas, such as helium, neon, an argon, and a xenon, nitrogen gas, etc. are mentioned, and these at least one sort is used, for example. Moreover, when using dilution gas, as for the rate of the gas for processing, it is desirable that it is one to 10 volume %.

[0051] In addition, it is advantageous, when the way of the compound which has many electrons as a controlled atmosphere (gas for processing) raises plasma density and high-speed processing is performed, as mentioned above. However, an argon or nitrogen is easy to receive and suitable at a cheap point.

[0052] As this invention was indicated to the claim 5, it is also desirable to improvement in the adhesion of a base material, a thin film, or thin films that a base material or at least one sort of thin films carry out plasma treatment to the field by which the laminating was carried out beforehand.

[0053] Although the atmosphere at the time of carrying out plasma treatment beforehand will not be limited especially if the above-mentioned base material and a thin film are not degraded remarkably, from a viewpoint of economical efficiency and safety, rare gas, such as helium, neon, an argon, and a xenon, nitrogen gas, etc. are mentioned, and these at least one sort is used, for example.

[0054] Since a process is not stabilized in order that electric discharge may arc-ize, if too high [when the applied voltage at the time of carrying out plasma treatment beforehand is too low, it has little improvement in the adhesion of a base material, a thin film, or thin films, and], in argon atmosphere, 1-2kV is 1.2-1.7kV desirable still more preferably, and 6-11kV is 7-8.5kV desirable still more preferably in nitrogen atmosphere.

[0055] Moreover, since plasma density will become high, a base material or a thin film will be deleted flat and smooth, if too high [when the frequency at the time of carrying out plasma treatment is too low, it has little improvement in the adhesion of a base material, a thin film, or thin films, and] and improvement in the adhesion of a base material, a thin film, or thin films decreases, in argon atmosphere or nitrogen atmosphere, 1-8kHz is 2-4kHz desirable still more preferably.

[0056] Furthermore, when it is too short, it has little improvement in the adhesion of a base material, a thin film, or thin films, and if too long, since a base material or a thin film is deleted flat and smooth and the improvement of required for plasma treatment time in the adhesion of a base material, a thin film, or thin films will decrease, in argon atmosphere or nitrogen atmosphere, 5-20sec is desirable [time].

[0057] The manufacture method of the surface treatment article of this invention introduces the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side. (Operation) When voltage build up time impresses and field strength impresses the pulse-ized 1-100kV [/cm] electric field 100 or less microseconds between the pressure near the atmospheric pressure, nothing, and a counterelectrode, while generating electric discharge plasma Since it continues, and a base material is stuck to one of opposite sides and passed between the aforementioned counterelectrodes, where the gas for processing was introduced between

counterelectrodes and made with the pressure near the atmospheric pressure. The pulse-sized electric field are impressed, by impressing predetermined pulse electric field to a counterelectrode, the electric discharge plasma depending on the aforementioned gas for processing occurs, and a thin film is formed in the base material which passes through the inside of this electric discharge plasma at the same time it generates the stable high-density plasma.

[0058] Here, a thin film is formed only in one side of a base material by running inter-electrode, without a base material flustering, making it stick to one of opposite sides, and making it pass by continuing a base material between counterelectrodes, and making it stick to one of opposite sides, and making it pass. By passing continuously two or more sets of counterelectrodes which changed the kind of gas made to exist between each counterelectrodes furthermore, the laminating of two or more thin films with various kinds of properties corresponding to the kind of gas can be carried out continuously simultaneously at high speed. Moreover, since it can process by the ordinary pressure, processing is performed under the pressure near the atmospheric pressure in equipment. The large-scale exhaust like [that it should just change the seal of the inlet of a base material and the exhaust port into the secret state of a grade where the leakage of a gas can be permitted] the processing performed by the vacuum system is not needed. Therefore, supply of a base material, change of a base material, and change of gas composition can be performed freely, and can manufacture various kinds of surface treatment articles economically.

[0059] Furthermore, when a base material or at least one sort of thin films carry out plasma treatment to the field by which the laminating was carried out beforehand, adhesion with the thin film in which it *****s and the front face of a base material or a thin film is newly formed of an anchor effect improves.

[0060]

[Embodiments of the Invention] The gestalt of the operation of this invention to the following is explained in detail, referring to a drawing. Drawing 3 is the ** type view showing an example of the equipment used for the manufacture method of the surface treatment article of this invention. As shown in drawing 3, the equipment used for this invention It mainly consists of the high-voltage pulse power supply sections 10 and 11, electric discharge plasma treatment equipments 20 and 21, a **** roll 80, and a taking over roll 81. each electric discharge plasma treatment equipments 20 and 21 Respectively, it consists of an parallel monotonous type counterelectrode (the up electrodes 30 and 31, lower electrodes 40 and 41), the gas supply sections 50, 51, 52, 53, 54, and 55 for processing, solid dielectrics 60, 61, 62, and 63, and the gas eccrisis sections 70 and 71 for processing.

[0061] Moreover, the up electrodes 30 and 31 are equipped with 60 and 61, and, as for the solid dielectric, the lower electrodes 40 and 41 are equipped with 62 and 63.

[0062] Various kinds of gas 90 and 91 for processing for between [every] the counterelectrodes (namely, 30/40, 31/41) of the adjoining electric discharge plasma treatment equipments 20 and 21 under the pressure near the atmospheric pressure Arbitrary kinds are chosen and introduced according to the purpose, and the pulse-sized electric field by above-mentioned conditions are impressed to each electrode. The electric discharge plasma according to the kind of gas for processing is generated, the base material 12 stuck to this by the solid dielectrics 60 and 61 of the up electrodes 30 and 31 is stuck, various kinds of thin films accumulate on the inferior surface of tongue of a base material 12, and the surface treatment article 13 is formed. The kind of gas 90 and 91 for processing introduced into each electric discharge plasma treatment equipments 20 and 21 changes with purposes, and even if, and it is different species, it is not cared about.

[0063] Heating and cooling systems 82 and 83 are adjacently formed in each electric discharge plasma treatment equipments 20 and 21, and a base material 12 has come be made to desired temperature. Of course, heating and a cooler style are included in the electric discharge plasma treatment equipments 20 and 21, and it does not matter as a temperature control being possible.

[0064] The seal of the electric discharge plasma treatment equipments 20 and 21 is carried out by the seal mechanism which is not illustrated, and they supply the gas 90 and 91 for after treatment which changed the inside of electric discharge plasma treatment equipment 20 and 21 into the reduced pressure state by vacuum pump P at the abbreviation vacua.

[0065] The gas which is supplied from the gas supply sections 50-55 for processing, and exists in

throughout [counterelectrode (namely, 30/40, 31/41)] needs to form a laminar flow on a base material 12, and the rate of flow needs to be almost uniform covering the processing width of face of a base material.

[0066] Drawing 4 shows an example of the gas supply sections 50-55 for processing, (A) is the cross section and (B) is the A-A cross section.

[0067] While the gas inlet 56 by which the gas supply pipe G is connected to the end section of the longitudinal direction of the direct rectangle-like gas supply section 50 for processing is formed By the ability forming [preparing two loculus in a longitudinal direction, and] the 1st room of a cam plate 14 on the diagonal line of 57 so that the 1st room may counter 57 in the gas introduction direction Form the partition which becomes so narrow that it keeps away from a gas inlet 56, and the reactant gas introduced from the gas inlet 56 is turbulent-flow-ized. abbreviation equalization of the density within the partition is carried out -- making -- the rate of flow -- abbreviation -- after deflecting the direction at the same time it considers as a uniform thing, it has the structure which rectifies gas and blows off from the stoma group 15 of uniform a large number prepared near the edge of 57 the 1st room

[0068] It is constituted so that can prepare 58 [room / 2nd], the gas which formed the slit 25 of uniform width of face near the marginal part, and came out of the 1st room of the stoma group 15 of 57 may turn around a diaphragm 24 in the 2nd room 58 while arranging the diaphragm 24 with which the gas which came out of the stoma group 15 is introduced and which has the uniform crevice 23 at the end, and it may become a laminar flow from a slit 25 and it may blow off to discharge space. Thereby, the flow of the gas which came out of the stoma group 15 is equalized.

[0069] Drawing 5 is the ** type view showing another example of the equipment used for the manufacture method of the surface treatment article of this invention. As shown in drawing 5 , the equipment used for this invention It mainly consists of the high-voltage pulse power supply sections 110 and 111, electric discharge plasma treatment equipments 120 and 121, a **** roll 180, and a taking over roll 181. A counterelectrode respectively coaxial-circles telescopic in each electric discharge plasma treatment equipments 120 and 121 (the up electrodes 130 and 131, lower electrodes 140 and 141), It consists of the gas supply sections 150 and 151 for processing, seal mechanisms 152, 153, 154, and 155, solid dielectrics 160 and 161, and the gas eccrisis sections 170 and 171 for processing.

[0070] Moreover, the lower electrodes 140 and 141 are equipped with solid dielectrics 160 and 161.

[0071] Various kinds of gas 190 and 191 for processing for between [every] the counterelectrodes (namely, 130/140, 131/141) of the adjoining electric discharge plasma treatment equipments 120 and 121 under the pressure near the atmospheric pressure Arbitrary kinds are chosen and introduced according to the purpose, and the pulse-ized electric field by above-mentioned conditions are impressed to each electrode. The electric discharge plasma according to the kind of gas for processing is generated, the base material 112 stuck to this by the up electrodes 130 and 131 is stuck, various kinds of thin films accumulate on a base material 112, and the surface treatment article 113 is formed.

[0072] Heating and cooling systems 182 and 183 are adjacently formed in each electric discharge plasma treatment equipments 120 and 121, and a base material 112 has come be made to desired temperature.

[0073] The seal of the electric discharge plasma treatment equipments 120 and 121 is carried out by the seal mechanism which is not illustrated, and the seal is carried out by the seal mechanisms 152, 153, 154, and 155, and they supply the gas 190 and 191 for after treatment which changed the inside of electric discharge plasma treatment equipment 120 and 121 into the reduced pressure state by vacuum pump P at the abbreviation vacua.

[0074] In addition, in this invention, although the high-pressure pulse power supply sections 10 and 11, 110, 111 are using the power supply which became independent to each of each electric discharge plasma equipment as shown in drawing 3 and drawing 5 , as long as the conditions which generate the electric discharge plasma in the method of this invention are satisfied, you may use a power supply in common.

[0075] moreover -- although the example which makes reduced pressure only the electric discharge plasma treatment equipments 20 and 21, 120, 121, and replaces them by the raw gas in drawing 3 and

drawing 5 was shown -- the **** rolls 80 and 180, the taking over rolls 81 and 181, and heating and cooling systems 82 and 83, 182, 183 -- all may be made reduced pressure and you may replace by the raw gas

[0076]

[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples. in addition -- the following examples -- as the high-voltage pulse power supplies 10 and 11 -- (-- use) was used for the Heiden lab company make, the product made from semiconductor device: IXYS, and part number IXBH40N160-627G

[0077] In the equipment shown in example 1 drawing 3, it considered as the manufacturing installation of a surface treatment article using what has the gas diffuser of the shape of a slit shown in drawing 4 as the gas supply sections 50-55 for processing. In addition, both the up electrodes 30 and 31 of electric discharge plasma treatment equipment and the lower electrodes 40 and 41 are sizes with a width-of-face 350x length of 150mm, and what coated the opposite side of two electrodes with the aluminum oxide with a thickness of 1.5mm by the spraying process as solid dielectrics 60-63 was used for them.

[0078] The base material 12 used the polyethylene-terephthalate film (it is called a "PET film" the Toray Industries, Inc. make, a tradename "lumiler T50", and the following) with a thickness [of 50 micrometers], and a width of face of 300mm, and it used it, having stuck it to the solid dielectrics 60 and 61 of the up electrodes 30 and 31.

[0079] The **** roll 80 and the winding roll 81 are minded [of the above-mentioned surface treatment article] for the PET film of a base material 12, and it is 10 kgf/m². Applying tensile stress by travel-speed 0.5 m/min After introducing into each electric discharge plasma treatment equipments 20 and 21 and setting the inside of electric discharge plasma treatment equipment 20 and 21 to 10Torr(s) by vacuum pump P, respectively, under the terms and conditions (field strength, frequency, discharge current density) shown in Table 1 The gas for processing excited with electric discharge plasma was contacted on one side of a PET film, and the surface treatment article was manufactured. In addition, the pulse-voltage wave made other conditions the wave (A) shown in drawing 1, 5 microseconds of build up time, and 70 microseconds of pulse width.

[0080]

[Table 1]

| | | |
|-----------------------------|----|----|
| プラズマ処理装置 | 20 | 21 |
| 電界強度(kV/cm) | 25 | 90 |
| 周波数(kHz) | 3 | 4 |
| 放電電流密度(mA/cm ²) | 2 | 3 |

[0081] The gas for processing moreover, from the gas supply sections 50-55 for processing to each inter-electrode one The argon gas which introduces by total-flow 15SLM and contains tetrapod isopropanol POKISHICHITANETO of 0.5 volume % in the gas supply sections 50-52 for processing, respectively, The nitrogen gas containing the tetrapod ethoxy silane of 0.5 volume % and the oxygen gas of 2 volume % is used for the gas supply sections 53-55 for processing. In the order of a laminating to a PET film, the thin film of titanium oxide (TiO₂) was made the 1st layer, the laminating of the thin film of oxidization silicon (SiO₂) was made to the 2nd layer, and the two-layer surface treatment article 13 of a PET film was manufactured.

[0082] (Example of comparison) The two-layer surface treatment article of a PET film was manufactured like the example 1 except not sticking a base material 12 to the solid dielectrics 60 and 61 of the up electrodes 30 and 31. The thin film was formed also in the rear face of a base material 12.

[0083] The refractive index of each thin film of the surface treatment article obtained in the evaluation (evaluation of thin film) example 1 of a surface treatment article and the example of comparison and thickness were measured using the ellipsometer (the MIZOJIRI OPTICAL Co., Ltd. make, form "BVA-36VW"). In addition, the thin film of the surface treatment article obtained in the example of comparison described the thickness of the sum total of the film formed in base-material

both sides. Furthermore, the two-layer surface treatment article of Above PET was arbitrarily cut to A4 edition, and the thickness homogeneity of each thin film was measured at 5mm interval using optical interference formula automatic thickness-measurement equipment (made in NANOMETO Rix Japan, form "M-5100").

[0084] (Reflection factor of a surface treatment article) The reflection factor of the surface treatment article obtained in the example 1 and the example of comparison was measured with the spectrophotometer (the Hitachi, Ltd. make, form "U-3000"), and it asked for the visible-ray average (wavelength of 400-700nm) reflection factor. The above result was collectively shown in Table 2.

[0085]

[Table 2]

| | | 実施例 1 | 比較例 | PET 744A |
|-----------|--------------------|-------|------|----------|
| 屈折率 | TiO ₂ 膜 | 2.13 | 2.13 | — |
| | SiO ₂ 膜 | 1.44 | 1.44 | |
| 膜厚 (nm) | TiO ₂ 膜 | 95 | 199 | — |
| | SiO ₂ 膜 | 128 | 27 | |
| 膜厚均一性 (%) | TiO ₂ 膜 | ±3 | ±15 | — |
| | SiO ₂ 膜 | ±3 | ±15 | |
| 反射率 (%) | | 0.2 | 2.0 | 7 |

It influences with [under base-material run] ****, and, as for the surface treatment article obtained in the example of comparison as shown in Table 2, the homogeneity of thickness is falling.

[0086] Examples 2-9 [0087] The gas shown in Table 3 was introduced until it was set to 760Torr(s) to electric discharge plasma treatment equipment 20, after setting the length of the lower electrodes 40 and 41 to 150mm and setting the inside of electric discharge plasma treatment equipment 20 and 21 to 0.1Torr(s) by hydraulic-pump P, respectively as the length of the up electrode 30 of the manufacturing installation of the above-mentioned surface treatment article was shown in Table 3, and this gas was introduced by 980SCCM after that. And under the terms and conditions (field strength, frequency) shown in Table 3, the gas for processing excited with electric discharge plasma was contacted on one side of a PET film. In addition, the pulse-voltage wave made other conditions the wave (A) shown in drawing 1, 5 microseconds of build up time, and 50 microseconds of pulse width. On the other hand, it introduced by 6 fluoride [propylene] 20SCCM and argon gas 980SCCM in electric discharge plasma treatment equipment 21, and the gas for processing which field strength, the frequency of 8kHz, and the pulse-voltage wave excited with electric discharge plasma by the wave (A) shown in drawing 1, 5 microseconds of build up time, and the conditions of 50 microseconds of pulse width was contacted on one side of a PET film. And plasma treatment of the PET film of a base material 12 was carried out by travel-speed 0.45 m/min through the **** roll 80 and the winding roll 81, and the surface treatment article 13 was obtained. In addition, the substantial processing time in electric discharge plasma treatment equipment 20 was combined and shown in Table 3.

[0088] The following examinations were presented after *(ing) the surface treatment article obtained in the evaluation examples 2-9 of a surface treatment article in 40 degrees C and the atmosphere of 95%RH for 1000 hours.

[0089] (Tape friction test) JIS The cross cut adhesion test was performed based on K5400, and the block count which has not exfoliated among 100 blocks was measured.

[0090] (The amount of carbon residues) The carbon content which remained to the tape surface of separation was analyzed by ESCA, and the detected carbon content was shown. In addition, interface adhesion becomes low, so that there are many carbon contents.

[0091] (Generating of a crack) The thin film layer was observed visually and the existence of generating of a crack was investigated. The above result was collectively shown in Table 3.

[0092]

[Table 3]

| 実施例 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|--------------|-----|-----|----------------|-----|-----|----------------|----------------|-----|
| 上部電極30長さ(mm) | 90 | 45 | 45 | 90 | 45 | 7.5 | 45 | — |
| ガス種類 | Ar | Ar | N ₂ | Ar | Ar | N ₂ | N ₂ | — |
| 印加電圧 (kV) | 1.7 | 1.5 | 8.0 | 0.8 | 1.0 | 8.0 | 12.0 | — |
| 周波数 (kHz) | 4 | 2 | 2 | 4 | 9 | 2 | 9 | — |
| 放電時間 (sec) | 12 | 6 | 6 | 12 | 6 | 1 | 6 | — |
| テープ剝離試験 | 100 | 100 | 100 | 90 | 80 | 73 | 90 | 70 |
| 残存炭素量(atm%) | 0 | 2 | 3 | 8 | 12 | 30 | 10 | 3.5 |
| クラックの発生 | 無 | 無 | 無 | 無 | 有 | 有 | 有 | 有 |

[0093] When examples 2-4 are compared with examples 5-9, by performing plasma treatment beforehand on condition that specification shows that the adhesion of a base material and a thin film layer becomes high, and generating of a crack is also lost so that clearly.

[0094]

[Effect of the Invention] Since the manufacture method of the surface treatment article of this invention is constituted as mentioned above, it can manufacture the surface treatment article which could produce the film continuously on one side of a base material, and was excellent in thickness and membraneous homogeneity under the pressure near the atmospheric pressure. Therefore, it can use for manufacture of various functional films, such as an antireflection film, an optical permselective membrane, an infrared reflective film, an antistatic film, an electromagnetic wave seal film, and semiconductor-device material, using the method of this invention.

[0095] Moreover, like the former, since it is not necessary to make the continuation manufacturing installation of the cascade screen of this invention into a reduced pressure system, its large-sized exhaust is unnecessary, and since carrying in and taking out of a raw material and a product become easy, it is very useful from the point of production operation nature and the economical efficiency of a production facility.

[0096] Furthermore, when a base material or at least one sort of thin films carry out plasma treatment to the field by which the laminating was carried out beforehand, adhesion with the thin film which newly produces a film improves.

[Translation done.]